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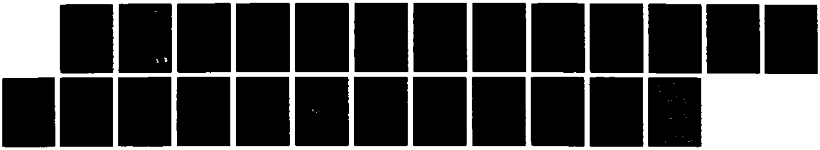

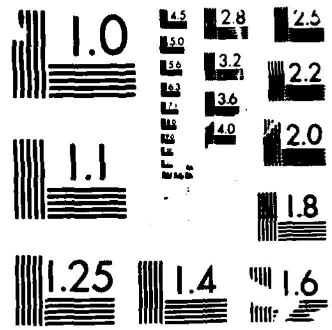

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Self-Absorption in Copper Hollow Cathode Discharges: Effects on Spectral Lineshape and Absorption Sensitivity

by

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Abstract

The intensity of the hyperfine doublet of the Cu I 324.8 nm transition was observed as a function of current, fill gas, and fill gas pressure for a new design of hollow cathode lamp incorporating a positive column and an enlarged volume cathode cavity. The intensity ratio of the two components, which reflects the degree of self-absorption, and the flame absorption sensitivity were compared with a conventional hollow cathode lamp. Higher intensity, better component ratio, and increased absorption sensitivity was found in the new lamp.

Introduction

Since the initial work by Paschen[1], and even after Walsh[2] proposed analytical atomic absorption spectroscopy, hollow cathode discharges have been spectroscopically studied in detail. As higher line intensity can give better signal/noise in atomic absorption and higher sensitivity in atomic fluorescence, many of the lamp improvements have been directed toward increasing the intensity of the resonant lines without sacrificing the line quality. Increasing the intensity in a conventional hollow cathode lamp by just increasing the current leads to broadening and later self-reversal of the resonant lines by self-absorption. The self-absorption of spectral lines has been thoroughly discussed by Cowan and Dieke[3].

Self-absorption broadening gives rise to rolloff in the analytical absorption curves with increased analyte concentration in an atomic absorption analysis. In the case of atomic fluorescence spectroscopy self-absorption is a less serious problem for the light source as long as the intensity of the central wavelengths can be increased. Increases in the non-absorbing intensity cause only a small negative contribution through increased scattered light level. This difference between AA and AF indicates that an optimum design of hollow cathode lamp for each technique may be different.

The aim of this research is directed toward increasing the line intensity without self-absorption broadening. To obtain high intensity and a lineshape which more or less matches the absorption profile of the flame

(i.e. without increasing the level of self absorption) it is necessary to eliminate the absorbing part of the discharge from the optical path.

These problems have been addressed by superimposing a boosted positive column discharge across the hollow cathode discharge[4-13]. The positive column feeds additional electrons into the hollow cathode plasma without increasing the sputtering. In fact, due to the boosting discharge the cathode fall decreases resulting in a reduction in the sputtering rate. This type of discharge provides the ability to control the metal atom and electron density independently while producing high intensity narrow lines for resonant transitions of a variety of elements. However, the boosted discharge lamp is complicated, consequently more expensive, and requires a special power supply.

This paper presents results obtained with a construction utilizing a small positive column in front of the cathode cavity to trap the sputtered metal atoms within the cathode hollow. The positive column segment further serves to pipeline electron flow and increases the level of excitation at the center of the cathode cavity. It also increases the electron density in the optical path preventing a buildup of cold unexcited atoms sputtered in front of the cathode hollow, which is the main cause of self reversal.

The lamp also contains an enlarged cathode hollow from which only the central region is sampled. Further benefits from such a cavity can be expected: the metal atom-electron density ratio, which mainly determines the excited and ground state atom densities, can be changed by changing the cavity shape. In fact, it is possible to decrease the sputtered metal atom density and increase the electron density in the central part of the

discharge. As this part is irradiated by the surrounding discharge regions, the density of the excited atoms can be increased at the expense of the ground state atoms by optical pumping.

The transition observed was the copper atomic resonant line $3d^{10}\,4p\ ^2P^o_{3/2} - 3d^{10}4s\ ^2S_{1/2}$ at 324.8 nm. This transition is complicated by isotope effects for Cu^{63} and Cu^{65} and hyperfine splitting of the transition[14]. At discharge temperatures, the twelve hyperfine lines form two components separated by approximately 0.4 cm^{-1}. When a Doppler temperature of 415 K was assumed and convoluted with their instrument function, Wagenaar and de Galan[15] calculated a peak component intensity ratio of 1.87:1.0 .

The example of these workers in giving the component intensity ratio as a measure of self-absorption is followed in this work. The ratio of these two components as a function of fill gas, pressure, and discharge current was observed and compared with a commercial hollow cathode lamp. It was expected that discharge conditions giving rise to the lowest component ratio would also yield the least sensitive analytical curves in the atomic absorption measurements. Plots of absorbed intensity are given as a measure of expected fluorescence signal from these lamps.

Apparatus.

Discharge Lamps.

The commercial hollow cathode lamp employed was a Westinghouse (Horseheads, NY) WL-22603 copper lamp with neon fill gas.

The hollow cathode lamps with added positive column (Hungarian patent application # 157/87) were of two constructions and are illustrated in figure 1. Both of these designs incorporate a floating potential metal disc in front of the cathode opening. This was designed to form the positive column in front of the cathode and also protected the front surface of the cathode against the discharge. The first design possessed an enlarged hollow cathode cavity, shown in figure 1 by solid lines. When the lamp proved superior to the conventional lamp a modification (shown by dotted lines) was made. Its cathode cavity was similar to a conventional hollow cathode lamp. With the second lamp it was shown that not only the positive column but also the enlarged cavity contributed to the lamp performance.

Line Profile Measurements.

Radiation from the discharge lamp under study was directed onto the entrance slit of a Zeiss PGS-2 monochromator by a UV achromat lens. The PGS-2 has a 2075 mm focal length and utilizes a grating of 650 grooves/mm blazed at 620 nm first order. The monochromator was operated in minus 8th order. The detector was an EMI 6256S photomultiplier and the lineshape was recorded on a chart recorder. Spectral quality helium and neon was used and

the tubes operated in DC discharge mode. Fill gas pressures were monitored with a Barocell pressure sensor.

Atomic Absorption Measurements.

Radiation from the discharge lamps was focussed on the analytical flame by a folding mirror and quartz lens. This radiation was refocussed by a second quartz lens onto the entrance slit of a Heath (Benton Harbor, MI) EU-700 monochromator. This 0.35 m focal length monochromator contains a grating of 1180 grooves/mm blazed at 250 nm. The photomultiplier on the monochromator was an Hammamatsu R212UH. PMT current was converted into voltage by a Keithley Instruments model 414 Micro-microammeter. This voltage formed the input signal for a Princeton Applied Research model 5101 Lock-in Amplifier. The discharge lamps output was chopped at 38 Hz by a Princeton Applied Research Model 125 Chopper. The analytical flame was air-acetylene from a circular multihole premix burner. This burner was chosen over a slot burner to minimize alignment problems.

Procedure

Lineshape Measurements.

Three lamp designs were evaluated in this study: a commercial hollow cathode lamp, a hollow cathode lamp with added positive column, and an enlarged hollow cathode cavity lamp with added positive column. The hollow cathode positive column lamp was operated at 3.75 torr of helium, and at

7.09 and 15.0 torr of neon. The enlarged cathode cavity lamp was studied with helium at 4.01 torr and neon at 5.74, 3.36, and 1.85 torr.

The doublet found by scanning over the 324.8 nm line of copper was analyzed as illustrated in figure 2. The height of the center of each peak was measured. The height of the longer wavelength (and most intense peak, in the absence of self-absorption) is given by I_L and the shorter wavelength peak by I_S. The ratio of these intensities was taken as a measure of the degree of self-absorption in the particular case. (A measure of the degree of self-reversal, given by the ratios $I_{ML} : I_L$ and $I_{MS} : I_S$, I_{ML} and I_{MS} being the peak maxima is published elsewhere[16].) The FWHM was also obtained from chart recorder traces during the lineshape measurements.

Atomic Absorption Measurements.

Copper solutions in 10% HNO_3 were prepared by dilution of 1000 ppm copper stock solution made by acid dissolution of Consolidated Wire and Associated Companies (Chicago, IL) copper wire. AA measurements were performed through an air-acetylene flame shielded by a slotted aluminum chimney. Performance of the commercial hollow cathode lamp was compared to that obtained with the enlarged cathode volume positive column incorporating lamp. The lamp was operated with gas pressures approximately the same as utilized in the lineshape measurements and allows comparison of the results of both studies.

Results

Lineshape Measurements.

Since several recent papers[8,15] deal with the lineshape measurements in copper hollow cathode discharges, this paper emphasizes the main differences between the positive column incorporating lamps and the conventional hollow cathode lamps. The detailed measurements of this study may be found elsewhere[16].

The degree of self-absorption is reflected in the intensity ratio of the two components since the more strongly emitting group is also more strongly absorbed. With increasing self-absorption in a homogeneously excited plasma, the ratio of the components approaches unity[17]. Ratio below unity usually means self reversal, but at least certainly shows a non-uniform plasma with an absorbing part in the optical path. The decreasing ratio is accompanied by an increasing width of the two components.

When Wagenaar and de Galan[15] compared hollow cathode lamps made by different manufacturers, they found that although different current was necessary to obtain the same intensity, a certain intensity always gave the same component ratio, i.e., the same level of self-absorption.

Figure 3 follows their example. In this figure the intensity ratio is plotted as a function of the intensity of the long wavelength peak. Helium fill gas gave a better intensity ratio and neon fill gave higher intensity at lower currents. At any fill gas pressure, the component ratio at the same intensity is higher for the positive column incorporating lamps than the conventional lamp. After measuring curves 1 and 2 and comparing with the Westinghouse lamp, a conventional hollow cathode lamp with the additional positive column was built. The measurements showed that both the

positive column and the the enlarged cathode cavity have contributed to the performance of the lamp.

Atomic Absorption Measurements.

Calibration curves made with the Westinghouse lamp and the positive column incorporating lamps were very similar, however the positive column lamp gave higher intensity and at the same intensities for both, higher absorbances were found with the positive column incorporating lamp. Figure 4 shows the absorbance as a function of lamp intensity where the two types of lamps are compared.

Since a better lineshape was found with the He filled discharge tube, better absorbance sensitivity was expected as well. However, the measured absorbances were similar to that found with the neon filled tube and much higher current was necessary to reach the same intensity.

Absorbed Intensities.

Part of the impetus for this research is to develop high intensity sources for atomic fluorescence spectroscopy. A measure of the expected fluorescence signal is given by the absorbed intensity and illustrated in figure 5. This figure gives similar information as figure 4, however, it also demonstrates the higher signal expected for the atomic fluorescence measurements.

It can be seen from the figure that the higher current gives higher absorbed energy. This of course is due to the increased intensity. The

small decrease of the absorption due to the increased intensity (see figure 4) in this respect is negligible.

Conclusions

An increase in the intensity of a hollow cathode light source has benefits for both atomic absorption and atomic fluorescence spectroscopy. This intensity increase is most useful if it can be obtained without self-absorption broadening of the spectral line.

These investigations indicate that incorporation of a confined positive column in front of the hollow cathode cavity is beneficial in this regard. With this construction, higher intensity at the same degree of self-absorption as the commercial hollow cathode lamp may be obtained. The positive column lamp with neon fill offers reasonable sensitivity for atomic absorption analysis at increased intensity and should prove to be useful for atomic fluorescence spectroscopy.

The enlarged cathode cavity lamp with positive column gave considerably different results than the hollow cathode lamp with positive column. Several differences due to the construction may be important. The current density at the cathode surface is lower in the enlarged volume case. The sputtered metal density in the region viewed is probably lower in the enlarged volume lamp as well, since only one surface (the backside of the cathode hollow) is adjacent to the central part of the plasma. The hollow cathode version not only has the back surface to contribute, but the immediately adjacent cylindrical bore as well. The external region which

surrounds the viewed region in the enlarged cathode volume lamp may enhance excitation in the viewed region of lower metal atom density by a radiation trapping effect. The importance of this region is being investigated through a series of lamps of varying cathode inner diameter and depth.

Further benefits may be attributed to the enlarged volume hollow cathode lamp. Since sputtered metal atoms go into the central part of the plasma mainly from the back surface of the cathode cavity, the metal atom density is low in this region. The electron density in the central part of the enlarged volume lamp, however, is higher than in a conventional hollow cathode lamp because it is operated at higher current and most of the total current flows through this part. On this point, the central region of the enlarged cathode volume lamp resembles a boosted discharge construction. The electron - atom density ratio in this region could be optimized by altering the size and shape of the cathode cavity.

The use of helium fill gas in the enlarged cathode volume lamp did not yield the increase in absorption sensitivity over neon that was expected from the linewidth measurements. This may be a result of collisional line shift in the absorption flame. The lamp utilizing neon exhibited slightly greater FWHM than with helium; this would lead to a greater degree of overlap of emission and absorption profile if collisional shifting had occurred. Such shifting in the air-acetylene flame has been studied[36].

The lamps have only two electrodes and require only one simple power supply. Better performance than a standard hollow cathode lamp is possible with these lamps at low currents, however, to obtain the full potential from

these lamps a power supply which supplies higher operating currents than a conventional hollow cathode lamp supply is necessary.

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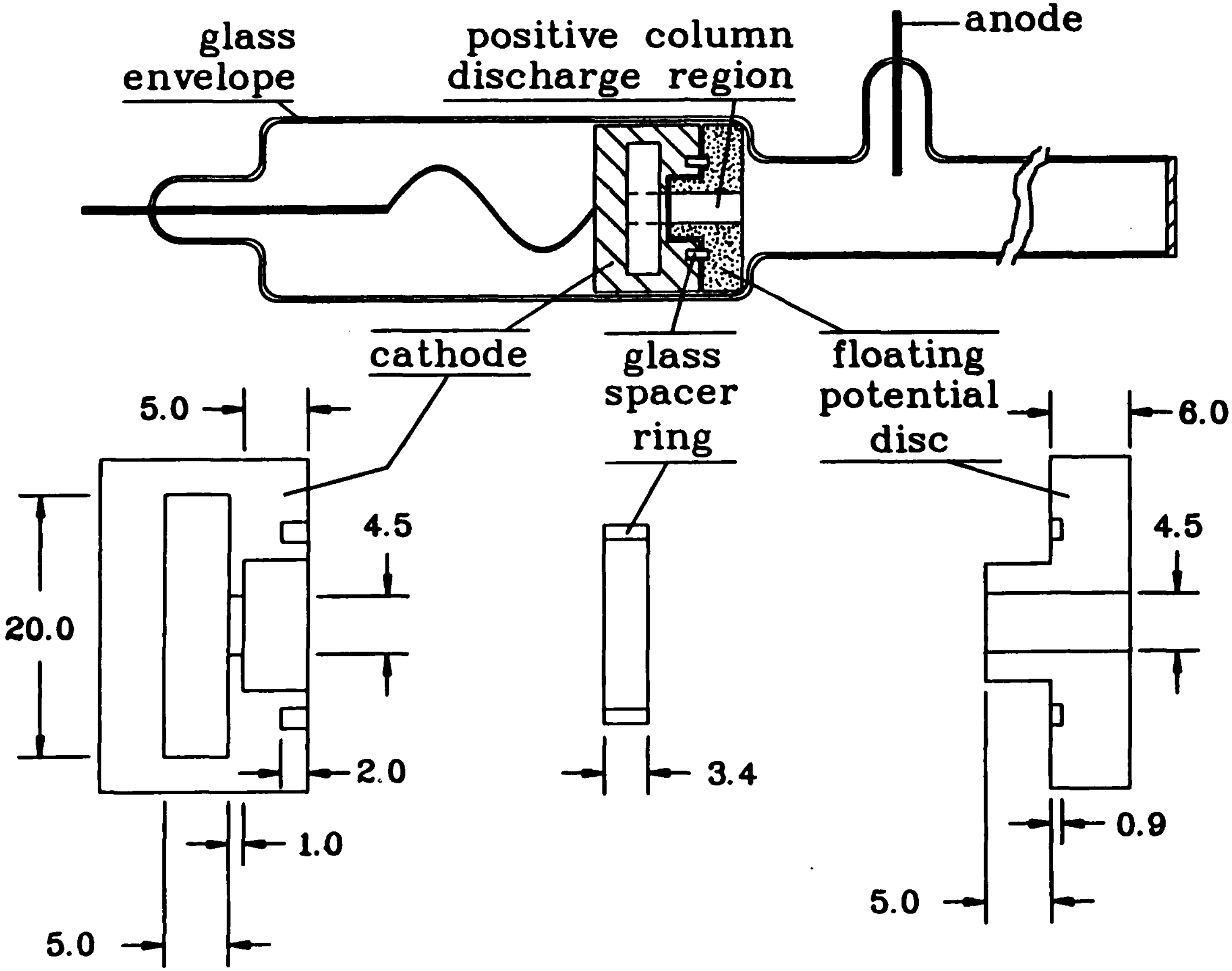
Bibliography

1. F. Paschen, Ann der Physik 50, 901 (1916).
2. A. Walsh, Spectrochim Acta 7, 108 (1955).
3. R. D. Cowan, and G. H. Dieke, Rev Mod Phys 20, 418 (1948).
4. J. V. Sullivan, and A. Walsh, Spectrochim Acta 21, 721 (1965).
5. R. M. Lowe, Spectrochim Acta 26B, 201 (1971).
6. Super Lamp, Photron Pty. Ltd., Dandenong, Victoria, Australia.
7. S. A. Myers, Spectrochim Acta 34B, 213 (1979).
8. D. K. Davies, J Appl Phys 38, 4713 (1967).
9. Z. van Gelder, Appl Spec 22, 581 (1968).
10. H. G. C. Human, P. J. Th. Zeegers, and J. A. van Elst, Spectrochim Acta 29B, 111 (1974).
11. J. V. Sullivan, and J. C. van Loon, Anal Chim Acta 102, 25 (1978).
12. J. V. Sullivan, Anal Chim Acta 105, 213 (1979).
13. G. S. Lomdahl, T. Norris, and J. V. Sullivan, Am Lab 15(3), 66 (1983).
14. P. Brix, and W. Humbach, Z Physik 128, 506 (1950).
15. H. C. Wagenaar, and L. de Galan, Spectrochim Acta 30B, 361 (1975).
16. H. A. Phillips, PhD thesis, University of Arizona, 1988.
17. A. I. Bodretsova, B. V. L'vov, and V. I. Mosichev, J Appl Spec 4, 149 (1966).

List of Figures

Figure 5. Absorbed intensity, IO - I, as a function of copper concentration for the Westinghouse hollow cathode lamp at maximum recommended operating current (20 mA) and for the enlarged cathode volume with added positive column lamp operated at 100-300 mA with 3.31 torr Ne fill.



glass envelope
positive column discharge region
anode
cathode
glass spacer ring
floating potential disc
5.0
20.0
4.5
2.0
1.0
5.0
3.4
6.0
4.5
0.9
5.0

Figure 1

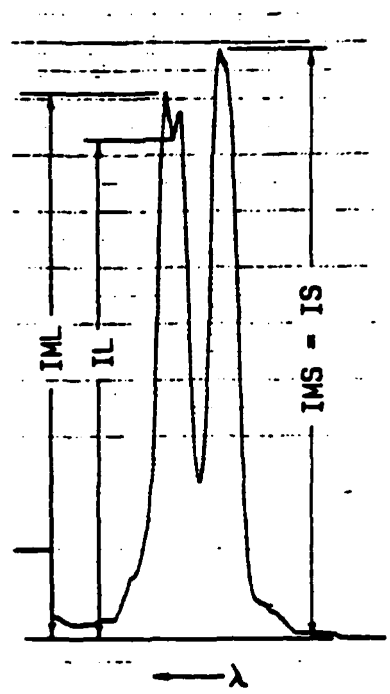
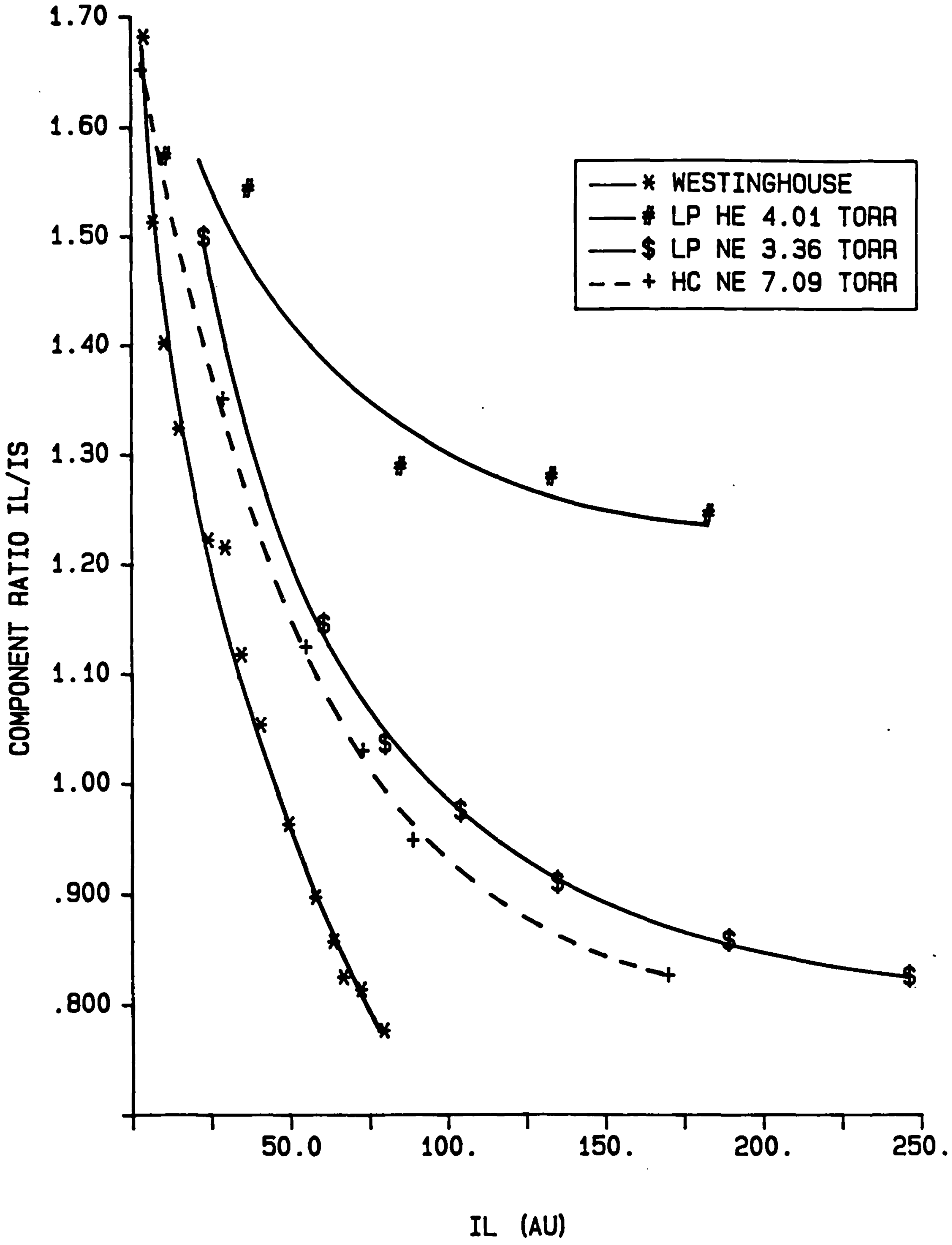
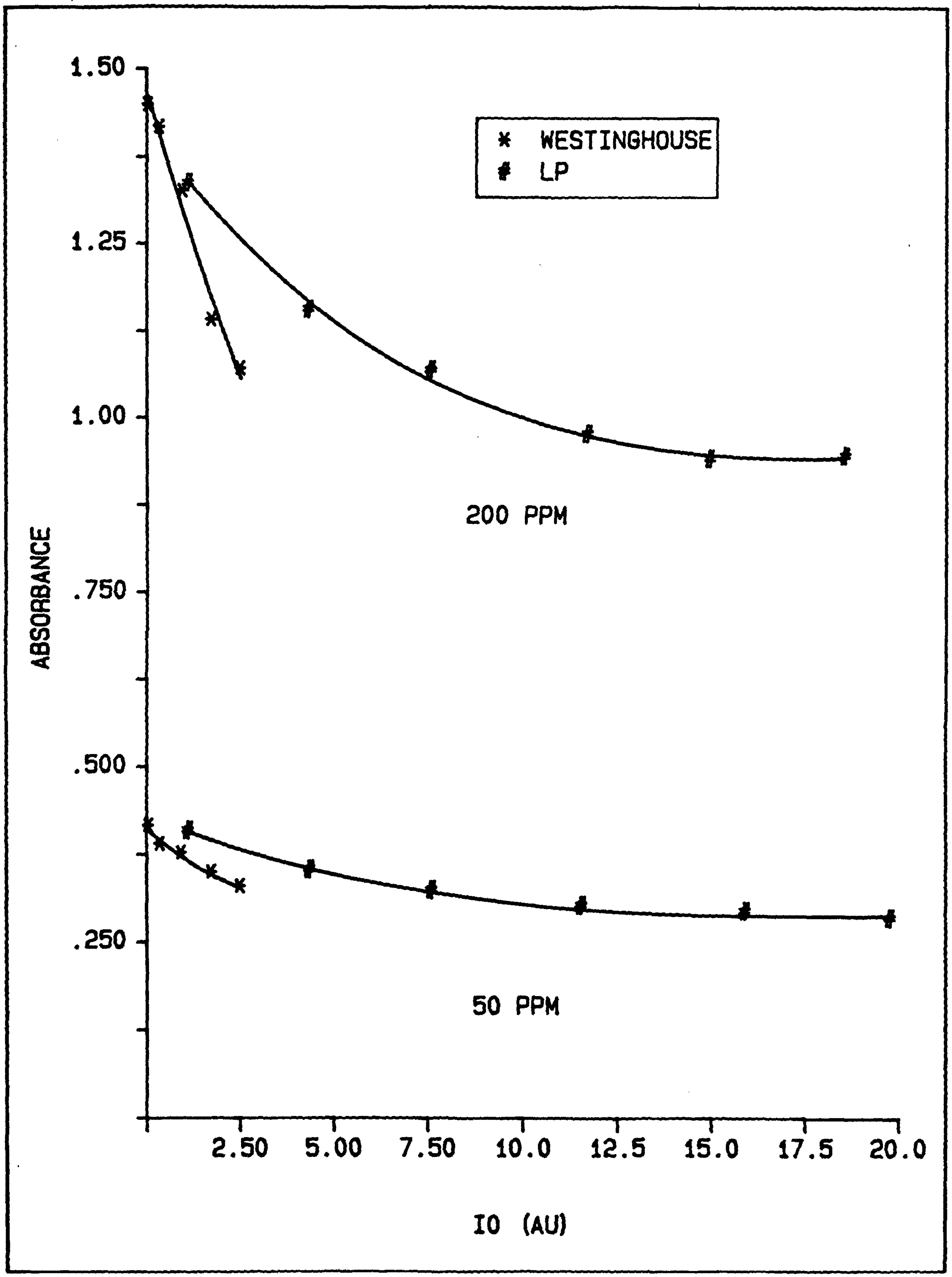


FIGURE 2.
~~Figure 5.~~ Definition of terms for the lineshape measurements. IL and IS are intensities at the peak center. IML and IMS are the peak maxima, different from IL and IS if there is self reversal.


WESTINGHOUSE
LP HE 4.01 TORR
LP NE 3.36 TORR
HC NE 7.09 TORR
COMPONENT RATIO IL/IS
IL (AU)
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
.900
.800
50.0
100.
150.
200.
250.



WESTINGHOUSE
LP
1.50
1.25
1.00
.750
.500
.250
ABSORBANCE
200 PPM
50 PPM
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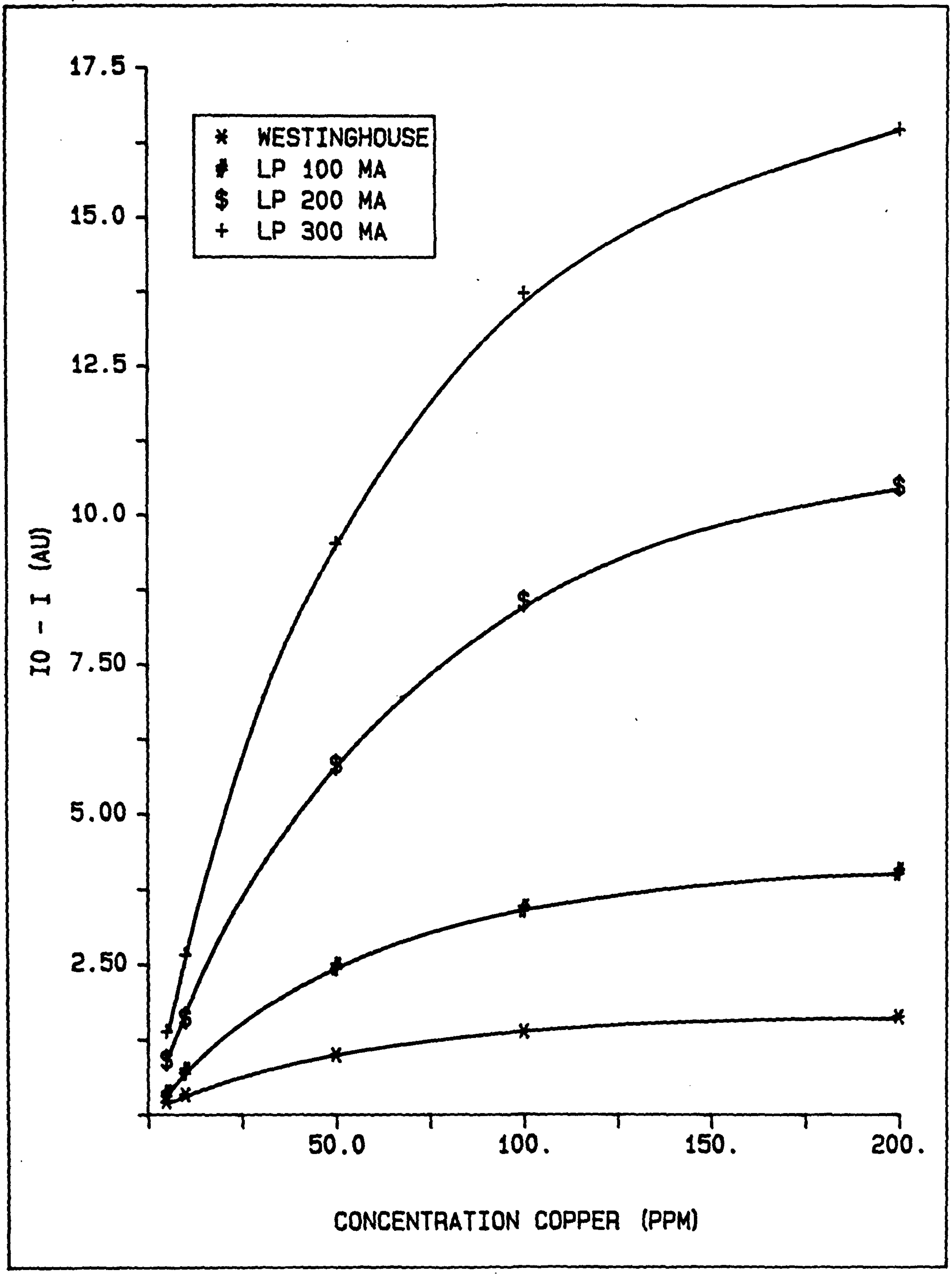
5.00
7.50
10.0
12.5
15.0
17.5
20.0
IO (AU)

Figure 4



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